

UDC 666.291.3:666.762.14(047)

## USE OF THE PRECIPITATION METHOD IN THE SYNTHESIS OF CERAMIC PIGMENTS

**I. V. Pishch<sup>1</sup> and E. V. Radion<sup>1</sup>**Translated from *Steklo i Keramika*, No. 6, pp. 37 – 39, June, 2005.

The results of the synthesis of ceramic pigments using coprecipitation of hydroxides and difficultly soluble salts of multivalent metal ions are described. The specifics of the coprecipitation process and the effect of various factors on the production of the initial precipitates for subsequent synthesis of ceramic pigments are analyzed. The technology of pigment production is described.

Technologies for producing ceramic pigments are constantly being upgraded. A promising method is coprecipitation of multicharge metal ions in the form of hydroxides with their subsequent separation from the solution, rinsing, drying, and calcination of the resulting precipitates.

Coprecipitation of hydroxides has several specifics. It is observed [1] that under coprecipitation of metal hydroxides, the precipitate is not a mechanical mixture of two hydroxides, since it has some properties not typical of the individual hydroxides. Metal hydroxides at the moment of coprecipitation can interact; in this case a “prestructure” of the future inorganic material arises in the form of an x-ray-amorphous hydroxy complex. Such “prestructure” easily transforms into the finished product at a lower temperature and a shorter heat-treatment duration; therefore, the hydroxide technology for producing inorganic materials, including pigments, has several advantages over the powder technology.

Our long-term systematic studies indicate that the method of coprecipitation of metal hydroxides is promising for the synthesis of ceramic pigments [2 – 14]. This method provides pigments with high chromophore parameters and thus decreases heat and energy consumption, since the synthesis of pigments from preliminarily obtained precipitates proceeds at a temperature lower by 100 – 200°C than the temperature of synthesis of pigments according to the traditional powder technology.

The purpose of the performed studies was to investigate the possibility of synthesis of pigments based on different systems by the precipitation method, to identify the optimum conditions for precipitation and heat treatment and determine the color characteristics of pigments, and to issue recommendations for their application.

To produce coprecipitated hydroxides, we used aqueous solutions of the following salts: copper (II), iron (III), chro-

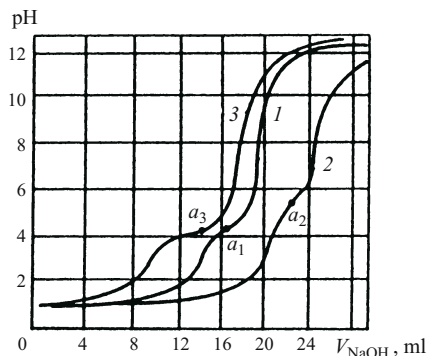
mium (III), cobalt (II), and strontium (II) nitrates, nickel (II), titanium (IV), zinc (II), cadmium (II), and iron (III) — ammonium sulfates, aluminum (III) and calcium (II) chlorides, zirconium (IV) oxychloride, and sodium silicate. The conditions of synthesis varied by the following parameters:

- the type of initial metal salts used for precipitating hydroxides, as well as introducing titanium (IV) and zirconium (IV) in the form of solutions of their salts and in the form of crystalline  $\text{TiO}_2$  and  $\text{ZrO}_2$ ;
- introduction of an additional component (sodium silicate) in the systems of coprecipitated hydroxides;
- the type of precipitator (aqueous solutions of  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{NH}_3$ );
- the salt : precipitator ratio and the ratio of the salt of  $\text{Me}^+$  to the salt of  $\text{Me}^{3+}$ ;
- sequence of precipitation (direct or reverse);
- concentration of salt solutions (0.1, 0.5, and 1.0 M) and precipitators (1 M, diluted 1 : 1, concentrated).

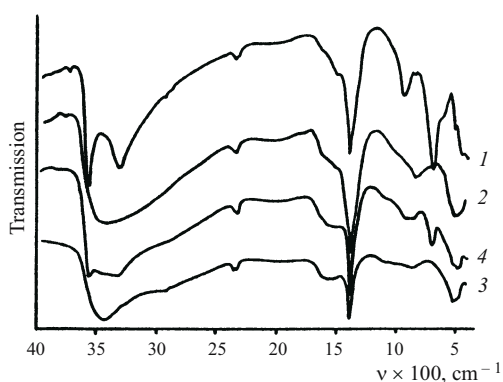
To determine the optimum pH values for precipitation and the required quantity of the precipitator, we performed pH-metric titration (ÉV-74 universal ionometer).

Taking the example of the  $\text{Al(III)} - \text{Cr(III)} - \text{NO}_3^- - \text{NaOH}$  system (Fig. 1), the variation of pH depending on the quantity of precipitator introduced is demonstrated. The pH curve of  $\text{Al(III)}$  titration with  $\text{NaOH}$  solution has two jumps, the first one corresponding to the back-titration of  $\text{HNO}_3$  at  $\text{pH} = 4.3$  (point  $a_1$ ) and the precipitation of aluminum hydroxide at  $\text{pH} = 7.7$ . In the titration of  $\text{Cr(III)}$ , first the acid forms of chromium (III) ions are back-titrated and then chromium (III) hydroxide is precipitated at  $\text{pH} = 7.7$ . During the coprecipitation of  $\text{Al(III)}$  and  $\text{Cr(III)}$ , a precipitate is formed in the interval of  $\text{pH} = 4.3 - 7.6$  containing both metals and constituting a mixed hydroxide. Similar results have been obtained for many other systems.

<sup>1</sup> Belarus State Technological University, Minsk, Belarus.



**Fig. 1.** Curves of pH-metric titration of solutions: 1) Al(III); 2) Cr(III); 3) Al(III) - Cr(III).



**Fig. 2.** IR absorption spectra of hydroxides: 1) copper (II); 2) chromium (III) - copper (II); 3) chromium (III); 4) mechanical mixture of chromium (III) and copper (II) hydroxides.

The data of pH alkali titration of solutions of Ti(IV) - Ni(II) - Zn(II) and TiO<sub>2</sub> - Ni(II) - Zn(II) systems point to chemical reactions between the components at the moment of formation of hydroxide precipitates; furthermore, individual hydroxides are not identified under the perovskite molar ratio of Ti : Me = 1 : 1, whereas in the case of a deviation from this ratio the excessive two-charge metal ions precipitate in the form of hydroxide.

It is established that in alkaline coprecipitation of ions whose hydroxides differ significantly in their acid-base properties, titanates are formed in the systems Ni(II) - TiO<sub>2</sub>, Ti(IV) - Ni(II) - Zn(II), and TiO<sub>2</sub> - Ni(II) - Zn(II), whereas

zirconates are formed in the systems Co(II) - Zr(IV), Co(II) - ZrO<sub>2</sub>, Ca(II) - Zr(IV), Sr(II) - Zr(IV), Cd(II) - Zr(IV), Ni(II) - Zr(IV), and Ni(II) - ZrO<sub>2</sub>.

In some cases metal ions react in the solution even before precipitation and form heteronuclear hydrocomplexes or exert a mutual effect on the hydrolytic properties of each other.

The sequence of pouring solutions is of great significance for the precipitation method. For instance, precipitates Cu(II) - Cr(III) were produced by direct and reverse pouring of solutions. It was found that the yield of precipitate is higher under the reverse order of pouring.

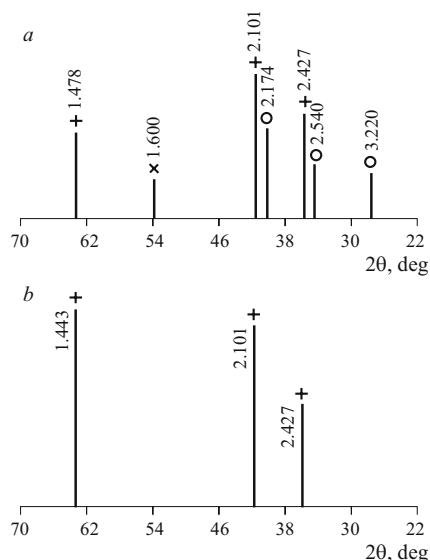
To study the structure and phase composition of pigments synthesized by the powder technology and by the coprecipitation method, x-ray phase analysis (DRON-2, DRON-3) and IR spectroscopy (UR-20, Specord-75 IR) were used. In most cases the IR spectra indicate that the products of coprecipitation of hydroxides are individual chemical compounds, including mixed hydroxides. Thus, the perceptible difference between the IR absorption spectra of chromium (III) hydroxide, copper (II) hydroxide, coprecipitated chromium (III) - copper (II) hydroxides, and a mechanical mixture of individual hydroxides (Fig. 2) is evidence of the probable interaction of hydroxides in the course of coprecipitation and the formation of a new chemical compound.

We also investigated the effect of the sequence of pouring solutions, the Me<sup>+</sup> : Me<sup>2+</sup> molar ratio, and heat treatment at different temperatures on the composition of reaction products. The diffraction patterns of pigments obtained by different methods based on different systems after firing exhibit reflections corresponding to spinels CoAl<sub>2</sub>O<sub>4</sub>, CuAl<sub>2</sub>O<sub>4</sub>, Fe<sub>2</sub>CuO<sub>4</sub>, CuCr<sub>2</sub>O<sub>4</sub>, and Cu<sub>2</sub>Cr<sub>2</sub>O<sub>4</sub>, corundum (Al, Cr)<sub>2</sub>O<sub>3</sub>, nickel ferrite NiFe<sub>2</sub>O<sub>4</sub>, strontium zirconate SrZrO<sub>3</sub>, and cadmium zirconate CdZrO<sub>3</sub>. For instance, under high-temperature synthesis of perovskite-type pigments based on the system Ni(II) - TiO<sub>2</sub>, the x-ray diffraction diagram of the calcined precipitate exhibits only the reflections belonging to NiTiO<sub>3</sub> with the perovskite structure (Fig. 3). At the same time, the pigments in some cases contain small quantities of free oxides. As the temperature grows, they interact and form solid solutions. X-ray phase analysis established that crystalline phases are formed more intensely when the samples are synthesized by the precipitation method.

The DTA results agree well with the data obtained by other methods and indicate the formation of new chemical compounds differing from individual hydroxides. As could be expected, substantial weight losses are registered in using the precipitation method. Apparently, in some cases (when the quantity of removed water deviates from the additive value) solid substitution solutions of hydroxides and perovskite-type solid solutions are formed in precipitation, and chemical reactions between hydroxides take place as well [14].

**TABLE 1**

| System   | Color of precipitate (visually) | Color of pigment depending on the temperature of synthesis |            |
|--|---------------------------------|--|------------|
|  |                                 | 800°C  | 1000°C     |
| Co(II) - ZrO <sub>2</sub>                                    | Brown                           | Dark blue  | Black      |
| Co(II) - ZrO <sub>2</sub> - Na <sub>2</sub> SiO <sub>3</sub> | Lilac                           | Light gray   | Dark gray  |
| TiO <sub>2</sub> - Ni(II) - Zn(II)                           | Bright green                    | Gray-green   | Dark green |
| Ni(II) - ZrO <sub>2</sub> - Na <sub>2</sub> SiO <sub>3</sub> | Bright lettuce                  | Light gray   | Lettuce    |
| TiO <sub>2</sub> - Co(II)                                    | Light brown                     | Light brown  | Dark brown |



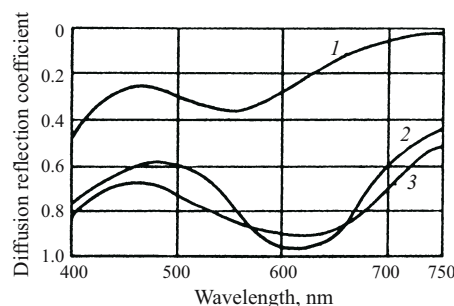
**Fig. 3.** Diffraction diagrams (Å) of  $\text{NiO} \cdot \text{TiO}_2$  samples produced by heat treatment of coprecipitated hydroxides (a) or by powder technology (b): +)  $\text{NiTiO}_3$ ; x)  $\text{NiO}$ ; O)  $\text{TiO}_2$ .

The chromophore properties of pigments significantly depend on their initial composition (chemical nature and concentration of colorant oxides). Thus, cobalt (II) can be used to produce black, dark gray, or dark brown pigments. The introduction of nickel (II) imparts characteristic dark green and lettuce tints to pigments, which is due to the presence of chromophores  $[\text{NiO}_4]$  and  $\text{Ni}_2\text{SiO}_4$ . The colorimetric parameters of some pigments are listed in Table 1.

Figure 4 shows the example of the  $\text{CoO} - \text{Al}_2\text{O}_3$  system with the spectral reflection curves of the precipitate, the pigment synthesized from this precipitate, and the tinted glaze coating.

The technology of producing pigments by the precipitation method includes the following operations: preparing solutions of initial components → volumetric proportioning → introduction of a precipitator → separation of the precipitate from the mother solution → rinsing of the precipitate → drying → firing → milling → packaging. The most energy-consuming operations of milling initial components are excluded. A decrease in the temperature of synthesis is achieved by firing finely dispersed amorphous hydroxide precipitates.

The proposed technology using the precipitation method makes it possible to obtain ceramic pigments of different crystalline structures with high chromophore parameters that can be applied to decorate porcelain, faience, and glass articles. Compared to powder technology, the temperature of synthesis can be decreased by 150–200°C and the unit power consumption reduced by 15–20%, while preserving high chromophore parameters.



**Fig. 4.** Spectral reflection curves of materials produced on the basis of  $\text{CoO} - \text{Al}_2\text{O}_3$  system: 1) coprecipitated hydroxide precipitate; 2) pigment; 3) tinted glaze coating.

## REFERENCES

1. V. P. Chalyi, *Metal Hydroxides (Formation Regularities, Structure, and Properties)* [in Russian], Naukova Dumka, Kiev (1972).
2. I. V. Pishch, T. L. Zalevskaya, and E. N. Putilina, "Synthesis of pigments by the precipitation method," *Steklo Keram.*, No. 3, 22–23 (1992).
3. I. V. Pishch, O. N. Chudnovskaya, E. N. Putilina, and N. I. Shabanova, "Production of pigments by the coprecipitation method," *Steklo Keram.*, No. 3, 21–22 (1993).
4. I. V. Pishch and E. V. Radion, "Production of pigments by the precipitation method," *Steklo Keram.*, No. 4, 20–21 (1995).
5. I. V. Pishch and E. V. Radion, "Pigment based on coprecipitated iron (III) and nickel (II) hydroxides," *Steklo Keram.*, No. 6, 19–20 (1996).
6. I. V. Pishch, E. V. Radion, D. M. Sokolovskaya, and N. F. Popovskaya, "Pigment based on coprecipitated chromium (III) and copper (II) hydroxides," *Steklo Keram.*, No. 7, 21–23 (1996).
7. I. V. Pishch and E. V. Radion, "Synthesis of pigments based on perovskite," *Steklo Keram.*, No. 9, 23–24 (1998).
8. I. V. Pishch and E. V. Radion, "Specifics of precipitation and formation of pigments in the titanium-nickel – zinc system," *Steklo Keram.*, No. 10, 17–19 (1998).
9. I. V. Pishch and E. V. Radion, "Production of pigments based on cobalt zirconate by the precipitation method," *Steklo Keram.*, No. 8, 23–25 (1999).
10. I. V. Pishch, N. F. Popovskaya, and E. V. Radion, "Synthesis of pigments based on the system  $\text{CuO} - \text{Cr}_2\text{O}_3 - \text{Al}_2\text{O}_3$  by the precipitation method," *Steklo Keram.*, No. 10, 23–25 (1999).
11. I. V. Pishch and E. V. Radion, "The effect of oxides on stabilization of zirconium dioxide," *Steklo Keram.*, No. 12, 27–29 (1999).
12. I. V. Pishch and E. V. Radion, "Production of pigments with perovskite-like structure based on nickel titanate by the precipitation method," *Steklo Keram.*, No. 5, 30–32 (2003).
13. I. V. Pishch and E. V. Radion, "Production of pigments with perovskite-like structure based on nickel zirconate by the precipitation method," *Steklo Keram.*, No. 2, 24–26 (2005).
14. I. V. Pishch and E. V. Radion, "Production of ceramic pigments by the precipitation method," in: *Publ. of Belarus State Technological University, Issue VIII* [in Russian], Minsk (2000), pp. 178–185.